

## Heteropoly Manganates as Oxidants: The Positional Effect of Mn(IV) on the Kinetics of Oxidation of D-glucose

T. JEYABALAN\*, R. MOHAN and A. NEPOLEAN RAJ

Department of Chemistry, Sacred Heart College (Autonomous)  
Tirupattur - 635601, India

### ABSTRACT

Rates of electron transfer reaction of D-glucose with the heteropolyanions,  $[\text{Mn}^{\text{IV}}\text{Mo}_9\text{O}_{32}]^{6-}$  and  $[\text{Mn}^{\text{IV}}\text{ThMo}_{12}\text{O}_{42}]^{4-}$  in aqueous medium have been studied spectrophotometrically at different temperatures. The order of the reaction with respect to substrate and oxidants has been studied. The activation parameters are evaluated from the data. The sodium perchlorate has no effect on the rate of the reaction. The formation of Mn(II) ions are identified using EPR spectral technique.

**Keywords:** Heteropolyanion, Manganese(IV), Positional effect, EPR, Kinetics.

### INTRODUCTION

Polyoxometalates have attracted much attention because of their structural versatility and use in different fields such as medicine, biology, catalysts and material science<sup>1-4</sup>. This is particularly so with heteropolyanions containing higher valent transition ion as heteroatoms. In contrast, Mn(IV) is present in a number of biologically important compounds<sup>5</sup>. Especially, it plays a vital role in photosystem(II) to produce molecular oxygen. Due to its interesting role in biological systems<sup>6</sup>, we have attempted to study the oxidizing property of Mn(IV) in two different environments, viz., the heteropolyanions,  $[\text{Mn}^{\text{IV}}\text{Mo}_9\text{O}_{32}]^{6-}$  and  $[\text{Mn}^{\text{IV}}\text{ThMo}_{12}\text{O}_{42}]^{4-}$  hereafter referred to as PA1 and PA2 respectively. D-Glucose has

been selected as the reductant due to its importance in food supply and metabolism. There are several investigations on the oxidation of D-glucose by metal complexes, but there is no report on the oxidation of D-glucose by heteropolymanganate(IV). In this paper, the kinetics and mechanism of D-glucose by PA1 and PA2 are presented.

### EXPERIMENTAL

#### Materials

PA1 and PA2 were synthesized according to the literature method.<sup>7,8</sup> Ammonium heptamolybdate, Thorium sulphate, manganese sulphate, sodium peroxy disulphate, sodium perchlorate and D-glucose were obtained from Qualigens, fine chemicals, India. All the chemicals were

of AR grade and used without further purification. Doubly distilled water was used for kinetic measurements. Sugar solutions were always used on the same day as made. Analar sodium perchlorate was used to study the effect of ionic strength.

### Synthesis of the compounds

The synthesis of PA1 was briefly outlined here. Aqueous solution of manganese sulphate (0.5g, 10 ml), containing the oxidant, sodium peroxy sulphate (0.2 g, 10 ml) was added to the solution of ammonium heptamolybdate (10 g, 100 ml) at 95° C. the resulting mixture was boiled for five minutes with constant stirring, quickly filtered and cooled. The orange-red crystals were recrystallised from hot water. The elemental analysis of the compound PA1 was given below.

#### PA1

Found: Mn, 3.49, Mo, 56.20.

$(\text{NH}_4)_6\text{MnMo}_9\text{O}_{32}$

requires Mn, 3.5; Mo, 56.14 %

The compound PA2 was prepared by mixing a solution of thorium sulphate (0.9g, 10 ml) to a boiling aqueous solution of ammonium molybdate (2.9g, 10ml) with stirring. To the resulting solution, aqueous solution of manganese sulphate (0.3g, 10ml) containing the oxidant sodium peroxy disulphate (0.4g, 10 ml) was added with continuous stirring. The resulting solution was filtered, cooled and saturated with ammonium nitrate to salt out the complexes, which were further purified by the recrystallisation from hot water. The elemental analysis of the compound PA2 was given below.

Found: Mn, 2.19, Th, 9.50; Mo, 48.01.

$(\text{NH}_4)_4[\text{MnThMo}_{12}\text{O}_{42}]\cdot 10\text{H}_2\text{O}$  requires Mn, 2.27; Th, 9.60; Mo, 47.64%

### Analytical and physical measurements.

Molybdenum was estimated gravimetrically as oxinates<sup>9</sup>. Manganese was estimated spectrophotometrically<sup>9</sup>.

#### a. EPR measurements

To ascertain the oxidation state of manganese, EPR spectra of these complexes, PA1 and PA2 were recorded. Also the  $d^3$  configuration of manganese in both PA1 and PA2 was verified also by back titration with potassium permanganate. EPR spectra of PA1 and PA2 were recorded on Varian E112 spectrometer. DPPH was used as an internal field marker.

#### b. Kinetic measurements

The kinetic measurements were made using Hitachi model 200-20 UV-Vis spectrophotometer having thermostatically controlled cell compartment. The disappearance of UV maximum at 340nm was followed for PA1, whereas for PA2 the UV maximum at 360nm was followed. pH measurements were made using Systronics 273pH meter. Several reaction mixtures with  $[\text{PA}] > [\text{Sugar}]$  at fixed sulphuric acid concentration were prepared. After the completion of the reaction the unreacted manganese which existed in the form of Mn(II) in acid solution was estimated spectrophotometrically. In all cases the stoichiometry was found to be 2:1 [PA: Sugar].

### c. Product analysis

One of the organic products, arabinose was identified by thin layer chromatography. A solvent mixture of 1-Butanol-acetic acid- water (4:1:5) was used and the detection was carried out by using iodine crystals. The other product formic acid was identified by treating the product with Zn/HCl followed by the addition of chromotropic acid<sup>10</sup>. The oxidation state of manganese changes from (IV) to (II) as probed by EPR spectroscopy EPR of the reaction mixture recorded at various time intervals from the time of mixing of reactants, showed increase in the intensity of Mn(II) signal with time (Figure 1).

## RESULTS AND DISCUSSION

### Characterisation of PA1 and PA2

PA1, a 9-heteropoly anion (Waugh type), has nine edge-sharing octahedra. In PA1, Mn(IV) is surrounded by six oxygen resulting in a MnO<sub>6</sub> octahedron<sup>7</sup>. In PA2, Mn(IV) is an axially distorted environment acting as a bridge between two heteropoly-molybdothorate moieties<sup>8</sup>. The structure is further confirmed by using EPR spectral techniques.

### EPR spectroscopy

The EPR spectrum of PA1(Figure 2) shows a weak signal at  $g = 4$  and a strong signal at  $g = 2$ . On the contrary, the PA2 shows strong signal (Figure 2) at  $g = 4$  and a weak signal at  $g = 2$  with manganese hyperfine coupling constant of 85 G, indicative of axially distorted environment around the manganese. In a crystal field,  $d^3$

ion with octahedral geometry has  $^4A_{2g}$  ground state, which gives an isotropic resonance at  $g = 2$ . Distortion and spin-orbit coupling split the ground quartet into two Kramer's doublets with the separation  $2(D^2 + 3E^2)^{1/2}$ , where D and E are axial and rhombic zero field splitting parameters<sup>11</sup>. Simplification occurs when the zero field tensor, D takes the limiting form  $2D \gg h\nu$  or  $2D \ll h\nu$ <sup>12</sup>. EPR spectrum of PA1 (Figure 2) reveals that the axial parameter D takes the limiting form  $2D \ll h\nu$ , as shown by weak signal at  $g = 4$  and a strong signal at  $g = 2$ .

The D value computed by using the equation

$$D = \sqrt{3/2} [(g\beta B_0)^2 - (2 g\beta B_{\min})^2]^{1/2}$$

is  $0.004 \text{ cm}^{-1}$  for PA1. For this calculation  $g$  (2.01) value of PA1 was used. The D value thus obtained is indicative of the almost perfect MnO<sub>6</sub> octahedron in PA1. The EPR spectrum of PA1 also shows hyperfine splitting at the region  $g=2$ , with the splitting constant  $A_{\text{Mn}} = 79.7 \times 10^{-4} \text{ cm}^{-1}$ . The calculated D value for PA2 is  $0.71 \text{ cm}^{-1}$ . The higher D value for PA2 is indicative of distortion from the octahedral geometry. The EPR spectrum of the compound PA2 shows hyperfine splitting in the region  $g=2$ . The signal shows six lines with splitting constant  $A_{\text{Mn}} = 76.1 \times 10^{-4} \text{ cm}^{-1}$ .

### Oxidation of D-glucose by PA1 and PA2

Kinetic measurements were carried out under pseudo-first order conditions,  $[\text{PA}] < [\text{D-glucose}]$ , in aqueous medium by spectrophotometric method. All the reactions followed first order kinetics as judged by the linearity of plots of  $\log$  (absorbance) versus time.

### Dependence on substrate concentration

The dependence of rate on substrate concentration was studied for both PA1 and PA2 at 30°C with [oxidant] =  $4.86 \times 10^{-4}$  mol dm<sup>-3</sup>, [H<sup>+</sup>] = 0.3 mol dm<sup>-3</sup> and [substrate] ranging from  $4.86 \times 10^{-3}$  mol dm<sup>-3</sup> to  $8.39 \times 10^{-3}$  mol dm<sup>-3</sup>. Plot of k versus [substrate] was linear with a slope of unity (shown in figure 3), showing first order dependence on the concentration of D-glucose (Table 1) in the reaction with PA1. The order in substrate was found to be non - integral for the oxidation by PA2. (Figure 4)

### Dependence on oxidant concentration

Mn(IV) species in acidic medium undergoes rapid protonation and becomes Mn(III)<sup>13</sup>. In the present case the colour of the Mn(IV) solution changed from reddish brown to light yellow, when sulphuric acid was added. In addition, the absorbance value was appreciably reduced and stood constant, when sulphuric acid was added to the PA1 solution. However, no appreciable shift in  $\lambda_{\text{max}}$  was observed. The decrease in the absorbance value showed with increase concentration of the sulphuric acid. This shows that the Mn(IV) species in acidic solution gets protonated and become Mn(III) species. The dependence of rate on oxidant was studied for both PA1 and PA2 at 30°C with [D-glucose] =  $4.86 \times 10^{-3}$  mol dm<sup>-3</sup>, [H<sup>+</sup>] = 0.2 mol dm<sup>-3</sup> (Table 2). Oxidation of D-glucose by PA1 shows a first order dependence on [PA1]. The rate constants show an initial increase followed by a decrease as the concentration of the oxidant is increased. This may be due to the formation of the complex between the

complex between the substrate and the polyanion containing the trivalent manganese (PA-Mn(III)). The concentration of the active species gets reduced by the complex formation. Similar behavior has been observed in the oxidation of formaldehyde by Mn(III) pyrophosphate, maleic acid by Mn(III) sulphate and citric acid by Mn(III) acetate<sup>14,15</sup>. The possible reactive species in sulphuric acid are Mn(OH)<sup>2+</sup>, Mn(HSO<sub>4</sub>)<sup>2+</sup>, Mn(SO<sub>4</sub>)<sup>+</sup>, Mn(SO<sub>4</sub>)<sup>2-</sup> and Mn(OH)<sub>3</sub>(HSO<sub>4</sub>)<sub>3</sub><sup>3-</sup> and their presence depends on experimental conditions<sup>15</sup>.

But in the present case, since Mn(III) ion is encircled by other MoO<sub>6</sub> moieties, the formation of above mentioned reactive species may not be possible. The formation of PA-Mn(III) substrate complex seems to be the probable reason for decrease in the rate as the concentration of the oxidant is increased. Added Mn(II) salt had no effect on the rate of oxidation, suggesting that PA having Mn(III) was not in equilibrium with Mn(II) species in the oxidation. However the reaction was found to go through free radical intermediate as confirmed by the polymerization of acrylonitrile in the system.

The rate of oxidation of D- Glucose by PA2 was low when compared to PA1 (Table 2). In PA1, the MnO<sub>6</sub> octahedron is surrounded by nine MoO<sub>6</sub> octahedra, whereas in PA2, the manganese is encircled by two [ThMo<sub>12</sub>O<sub>42</sub>]<sup>4-</sup> units. Hence the approach of reductant towards manganese and PA2 will be difficult. Therefore the rate of oxidation of D-glucose by PA2 may be low when compared to that of PA1.

### Dependence on [H<sup>+</sup>]

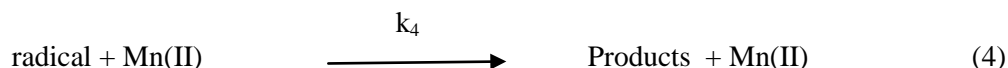
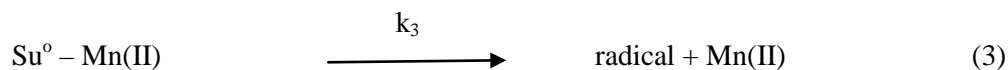
Acid dependence was carried out for both PA1 and PA2 with [oxidant] =  $4.86 \times$

$10^{-4} \text{ mol dm}^{-3}$ ,  $[\text{D-glucose}] = 4.86 \times 10^{-4} \text{ mol dm}^{-3}$  and  $[\text{H}^+] = 0.2 - 1.5 \text{ mol dm}^{-3}$  at  $30^\circ\text{C}$  (Table 3). The increase in the rate of oxidation of glucose with increase in  $[\text{H}^+]$  in the reactions may be due to the formation of PA-Mn(III) species. The plot of  $k$  versus  $[\text{acid}]$  for PA1 is given in the Figure 5. When the pH of the solution is above 4, the anion (PA1) is completely deprotonated. On the contrary, if the pH of the solution is below 4, the anion exists as two forms in the aqueous solution, viz  $[\text{H}_m\text{MnMo}_9\text{O}_{32}]^{(6-m)-}$  and  $[(\text{M})_n\text{H}_p\text{MnMo}_9\text{O}_{32}]^{(6-p-n)-}$ . The highly protonated species acts as active species in the aqueous solution. Since at higher acid concentration, the formation of protonated species increases, this increases the rate of a

reaction for PA1.

Whereas in PA2,  $\text{MnO}_6$  octahedron is encircled by two hetroopoly molybthorate moieties. Hence, the formation of protonated species is hindered. So the rate of the reaction is less as compared to that of PA1. The plot of  $k$  versus  $[\text{acid}]$  for PA2 is given in the Figure 6. Although the Mn(III) species in aqueous solution is not stable at neutral pH, it is stabilized in sulphuric acid. So the formation of stable PA-Mn(III) is favoured as the concentration of sulphuric acid is increased. The same trend is observed in the oxidation of phenacyl bromides by manganese (III) acetate. Added sodium perchlorate has no effect on the rate of the reaction.

Based on the experimental evidences, a possible mechanism may be proposed.



### Scheme 1

The step I may be rate- determining for PA1, whereas the step 2 may be slow step for PA2.

**Activation parameters**

The effect of temperature on the rate of the reaction was studied at 30, 35 and 40 °C and  $\Delta H^\ddagger$  and  $\Delta S^\ddagger$  were evaluated from the data (Table 4). Increase of temperature accelerates the rate of the reaction indicating the formation of a stable activated complex.

The negative value of  $\Delta S^\ddagger$  indicates the orderliness of the reaction and the formation of more rigid activated complex. The high value of  $\Delta H^\ddagger$  for PA2 indicates the difficulty in the formation of activated complex whereas in PA1 the formation of activated complex is easier, which is in accordance with earlier discussion.

**Table 1. Effect of [Reductant] variation on rate of the reaction.**  
[Oxidant] =  $4.86 \times 10^{-4} \text{ mol dm}^{-3}$ ,  $[\text{H}^+] = 0.3 \text{ M}$ ,  $T = 30^\circ \text{ C}$ .

[Reductant] x $10^3/\text{mol dm}^{-3}$	$k_1 \times 10^3/\text{s}^{-1}$ for PA1	[Reductant] x $10^3/\text{mol dm}^{-3}$	$k_1 \times 10^5/\text{s}^{-1}$ for PA2
4.86	$1.17 \pm 0.03$	4.86	$8.88 \pm 0.06$
5.74	$1.32 \pm 0.02$	5.17	$9.53 \pm 0.01$
6.62	$1.55 \pm 0.04$	6.21	$10.21 \pm 0.06$
7.51	$1.79 \pm 0.05$	6.97	$10.91 \pm 0.04$
8.39	$1.95 \pm 0.02$	7.96	$11.91 \pm 0.04$
8.92	$2.12 \pm 0.04$	8.96	$12.49 \pm 0.01$
9.65	$2.35 \pm 0.02$	9.65	$13.08 \pm 0.02$

**Table 2. Effect of [Oxidant] variation on rate of the reaction.**  
[Reductant] =  $4.86 \times 10^{-3} \text{ mol dm}^{-3}$ ,  $[\text{H}^+] = 0.3 \text{ M}$ ,  $T = 30^\circ \text{ C}$

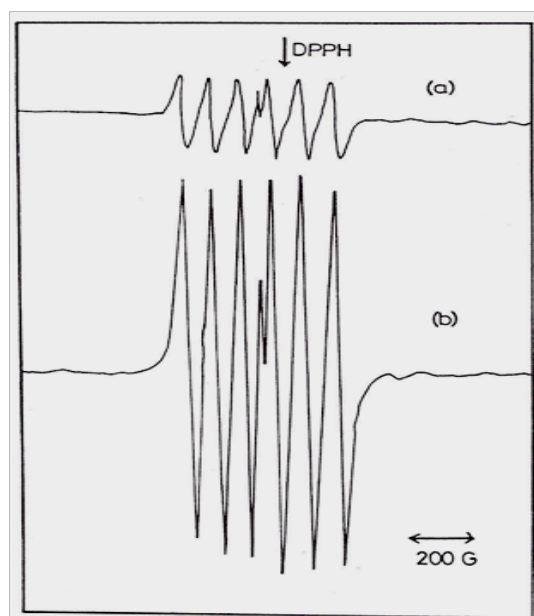
[PA1] x $10^4/\text{mol dm}^{-3}$	$k_1 \times 10^5/\text{s}^{-1}$	[PA2] x $10^4/\text{mol dm}^{-3}$	$k_1 \times 10^5/\text{s}^{-1}$
4.86	$9.69 \pm 0.04$	4.86	$9.67 \pm 0.03$
5.13	$9.94 \pm 0.03$	5.13	$9.91 \pm 0.04$
5.50	$11.14 \pm 0.04$	5.50	$11.11 \pm 0.04$
5.92	$10.50 \pm 0.05$	5.92	$10.40 \pm 0.03$
6.72	$9.58 \pm 0.04$	6.72	$9.56 \pm 0.03$
7.22	$9.25 \pm 0.04$	7.22	$9.23 \pm 0.04$
8.0	$8.65 \pm 0.05$	8.0	$8.63 \pm 0.02$

**Table 3. Effect of varying acid strength on rate of the reaction.**  
**[Oxidant] =  $4.86 \times 10^{-4}$  mol dm $^{-3}$ , [Reductant] =  $4.86 \times 10^{-3}$  mol dm $^{-3}$ , T = 30° C**

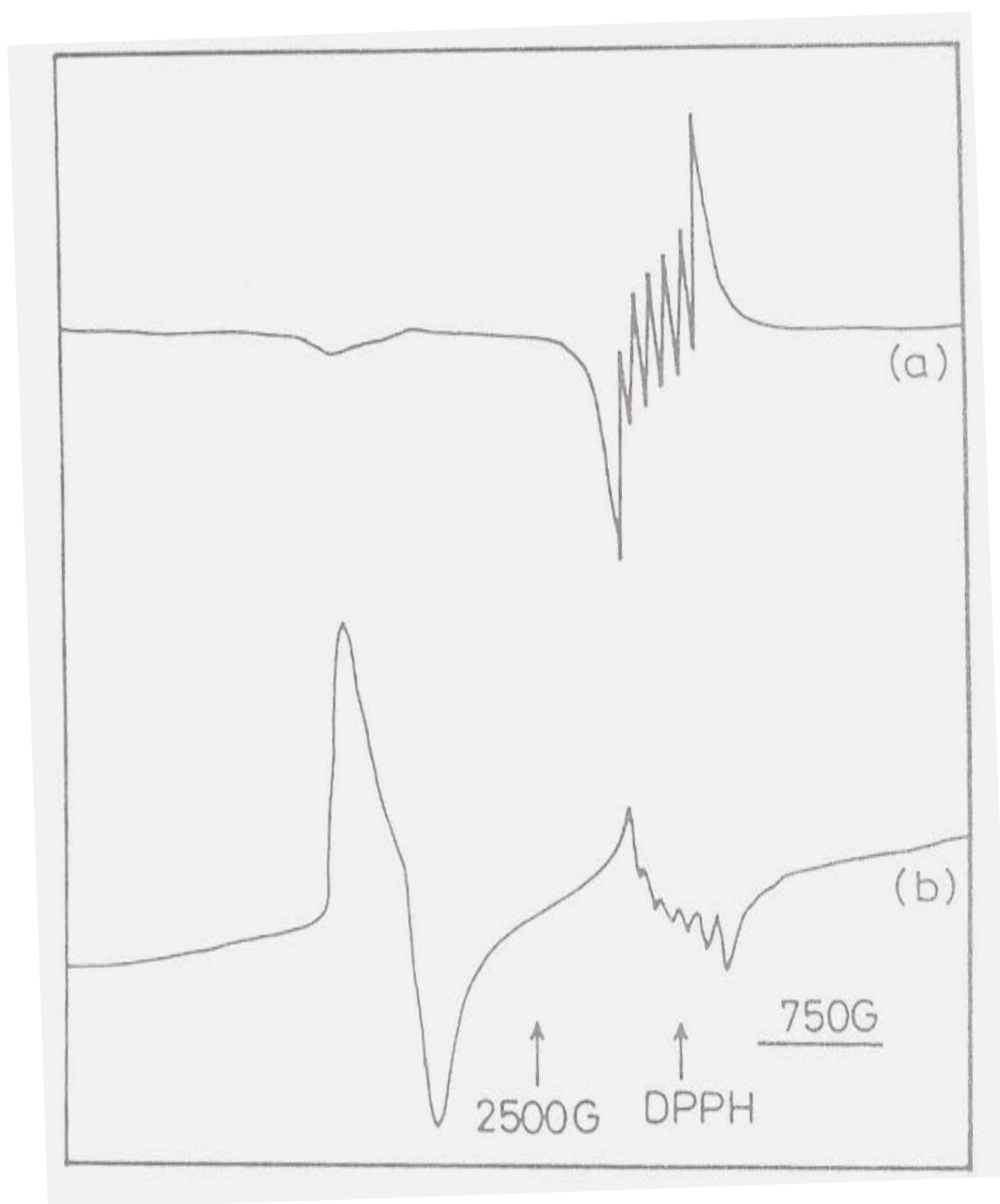
[H <sup>+</sup> ] /mol dm $^{-3}$	$k_1 \times 10^3$ / s $^{-1}$ for PA1	[H <sup>+</sup> ] /mol dm $^{-3}$	$k_1 \times 10^4$ / s $^{-1}$ for PA2
0.2	$1.2 \pm 0.02$	0.3	$0.88 \pm 0.02$
0.3	$1.4 \pm 0.03$	0.7	$2.51 \pm 0.02$
0.4	$2.1 \pm 0.03$	1.0	$3.77 \pm 0.04$
0.5	$3.0 \pm 0.04$	1.3	$5.01 \pm 0.03$
0.7	$4.5 \pm 0.03$	1.5	$6.29 \pm 0.04$
0.9	$5.7 \pm 0.04$		

**Table 4. Effect of temperature on the rate of the reaction and activation parameters.**  
**[Oxidant] =  $4.86 \times 10^{-4}$  mol dm $^{-3}$ , [Reductant] =  $4.86 \times 10^{-3}$  mol dm $^{-3}$ , [H<sup>+</sup>] = 0.3M.**

Temp K	$k_1 \times 10^4$ /s $^{-1}$ (PA1)	$\Delta H^\ddagger$ / kJ mol $^{-1}$ (PA1)	$\Delta S^\ddagger$ / JK $^{-1}$ mol $^{-1}$ (PA1)	$k_1 \times 10^5$ /s $^{-1}$ (PA2)	$\Delta H^\ddagger$ / kJ mol $^{-1}$ (PA2)	$\Delta H^\ddagger$ / kJ mol $^{-1}$ (PA2)
303	$8.06 \pm 0.02$	46.4	172.1	$6.47 \pm 0.03$	78.7	45.4
308	$11.70 \pm 0.1$	46.4	172.2	$8.88 \pm 0.02$	78.4	46.7
313	$20.90 \pm 0.1$	46.3	169.2	$17.5 \pm 0.01$	78.4	46.0



**Figure 1. X-band EPR solution spectra of the product Mn(II), as a function of time**  
**(a) after 5 minutes and (b) after 10 minutes.**



**Figure 2. X-band polycrystalline EPR spectra of Mn(IV) in  $[\text{MnMo}_9\text{O}_{32}]^{6-}$  (a) and  $[\text{MnThMo}_{12}\text{O}_{42}]^{4-}$  (b) at 300 K.**



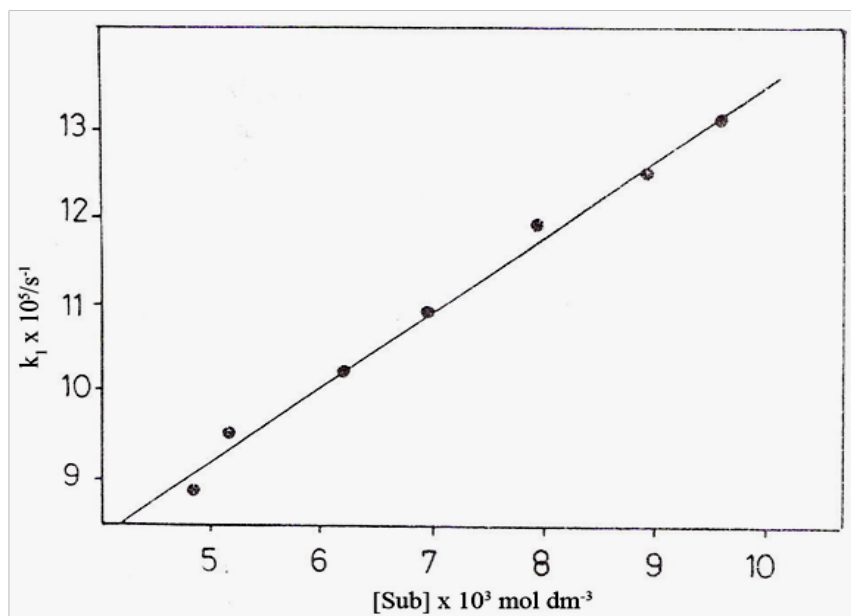


Figure 3. Plot of  $k$  versus substrate concentration for  $[\text{Mn}^{\text{IV}}\text{Mo}_9\text{O}_{32}]^{6-}$ . Other conditions:  $[\text{reductant}] = 4.86 \times 10^{-3} \text{ mol dm}^{-3}$ ,  $[\text{H}^+] = 0.3 \text{ mol dm}^{-3}$  and  $T = 30^\circ \text{C}$

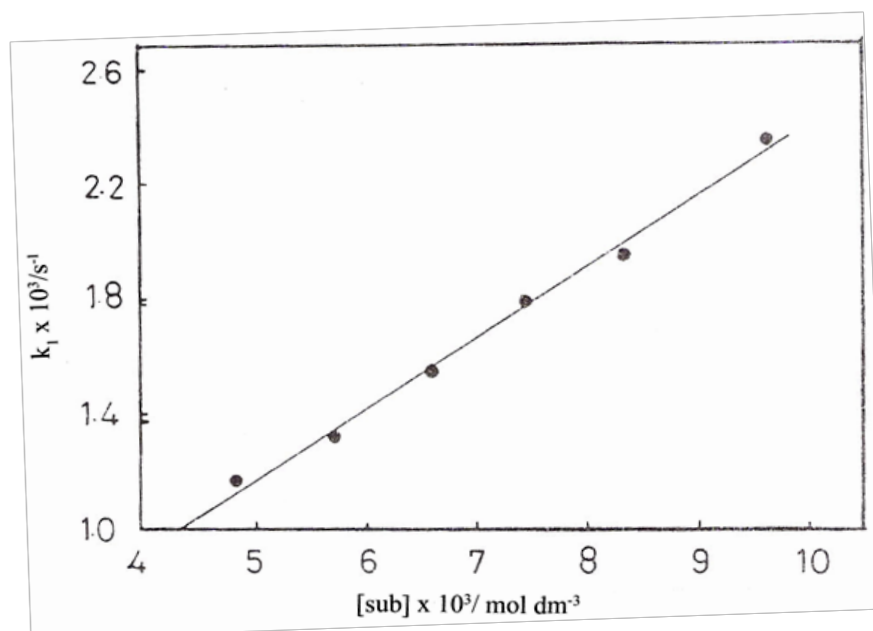


Figure 4. Plot of  $k$  versus substrate concentration for  $[\text{Mn}^{\text{IV}}\text{ThMo}_{12}\text{O}_{42}]^{4-}$ . Other conditions:  $[\text{reductant}] = 4.86 \times 10^{-3} \text{ mol dm}^{-3}$ ,  $[\text{H}^+] = 0.3 \text{ mol dm}^{-3}$  and  $T = 30^\circ \text{C}$

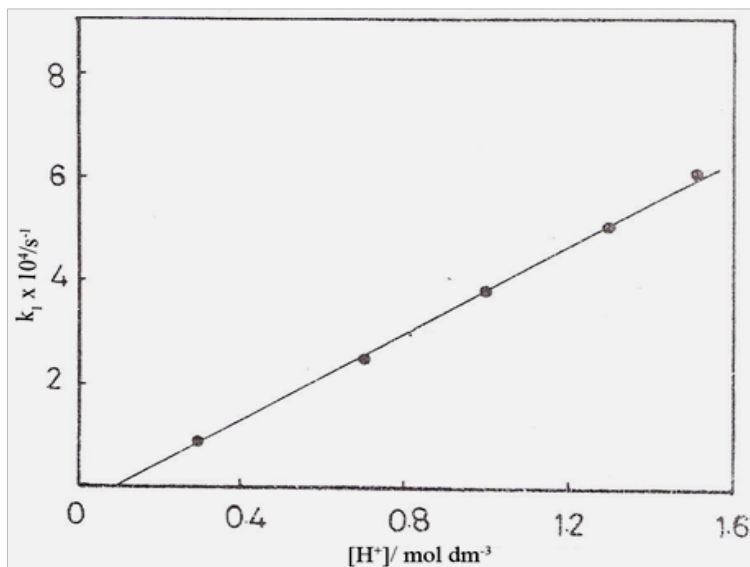


Figure 5. Plot of  $k$  versus acid strength concentration for  $[\text{Mn}^{\text{IV}}\text{Mo}_9\text{O}_{32}]^{6-}$ . Other conditions: [reductant] =  $4.86 \times 10^{-3} \text{ mol dm}^{-3}$ , [oxidant] =  $4.86 \times 10^{-4} \text{ mol dm}^{-3}$  and  $T = 30^\circ \text{C}$

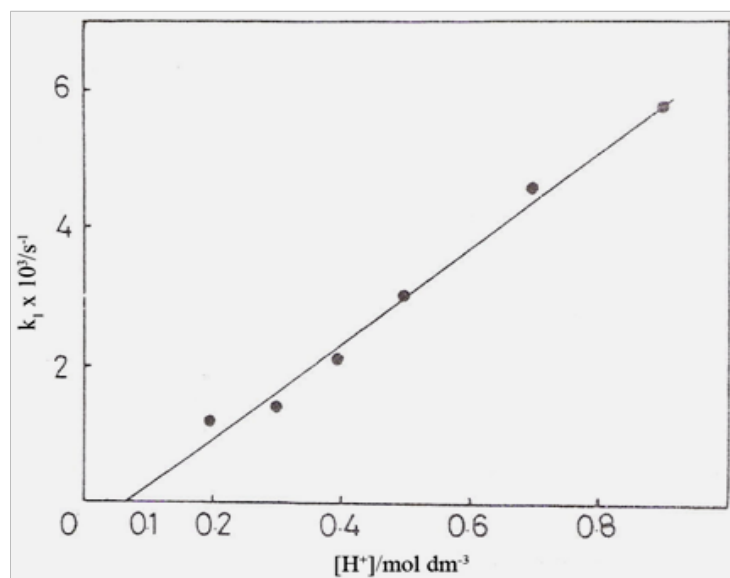


Figure 6. Plot of  $k$  versus acid strength concentration for  $[\text{Mn}^{\text{IV}}\text{ThMo}_{12}\text{O}_{42}]^{4-}$ . Other conditions: [reductant] =  $4.86 \times 10^{-3} \text{ mol dm}^{-3}$ , [oxidant] =  $4.86 \times 10^{-4} \text{ mol dm}^{-3}$  and  $T = 30^\circ \text{C}$

## CONCLUSION

The compounds PA1 and PA2 undergo one electron reduction with D-glucose in aqueous medium at different temperatures. The one electron transfer proceeds through free radical mechanism. For the reduction of 2 moles of HPA, 1 mole of D-glucose is consumed. The organic products are arabinose and formic acid. Order with respect to PA1 is one and order with respect to [D-glucose] is also one. For PA2, the order with respect to oxidant is one and order with respect to [D-glucose] is non-integral.

## ACKNOWLEDGEMENTS

The author thanks SAIC, IIT, Chennai for EPR spectral measurements and also UGC, New Delhi for financial support.

## REFERENCES

1. M. Gupta, S.K Saha and P. Banerjee, *J. Chem. Soc., Perkin Trans. II.*, 1781(1988).
2. S. K. Saha, P. Bhattacharya, A. Mohammad and P. Banerjee, *Bull. Chem. Soc. Jpn.*, 62, 3320 (1989).
3. M. T, Pope *Heteropoly and Isopoly Oxometalates*; Springer Verlag: Berlin, (1983).
4. Fengyan LinXu, W. Wang and E. Wang, *J. Mol. Struct.*, 61,753 (2005).
5. O. L. Chapman, C .C. Chang, and H. Tomika, *J. Am. Chem. Soc.*, 97, 6588 (1975).
6. A .White, P. Handler and E. L. Smith, *Principles of Biochemistry*, New York: McGraw Hill, 417 (1986).
7. T. Jeyabalan, *J. Chem & Chem. Sci.*, 103,1 (2011).
8. R. Murugesan, P.Sami, T.Jeyabalan and A. Shunmugasundaram, *Proc. Ind. Acad. Sci. (Chem.Sci.)*, 110,7, (1998).
9. Vogel A I, *A Text book of Quantitative Inorganic Analysis*, ELBS: Fourth Edn.; London, (1978).
10. K. R. Dhar, *Indian J. Chem.*, 31A, 97 (1992).
11. S. K. Chandra, P. Basu and A. Chakravorthy, *Inorg. Chem.*, 29, 2423 (1990).
12. S. Pal, P. Ghosh and A. Chakravorthy, *Inorg. Chem.*, 24, 3704 (1985).
13. A. Saito, H. Tomari and G. R. Choppin, *Inorg. Chim. Acta*, 258, 145(1997).
14. Guru Prasad, *Bull. Chem. Soc. Jpn.*, 38, 882(1965).
15. B. Hari Krishnan and E. V. Sundram, *Indian J. Chem.*, 28A, 793 (1989).